

## Stable Isotopic Variability within Modern Travertines

### La variabilité spatiale des teneurs isotopiques à l'intérieur des travertins modernes

### Dauerhafte isotopische Variabilität innerhalb der modernen Travertine

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Volume 48, numéro 3, 1994

Les travertins  
Travertines

URI : <https://id.erudit.org/iderudit/033007ar>

DOI : <https://doi.org/10.7202/033007ar>

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Éditeur(s)

Les Presses de l'Université de Montréal

ISSN

0705-7199 (imprimé)

1492-143X (numérique)

[Découvrir la revue](#)

Citer cet article

Chafetz, H. S. & Lawrence, J. R. (1994). Stable Isotopic Variability within Modern Travertines. *Géographie physique et Quaternaire*, 48(3), 257–273.  
<https://doi.org/10.7202/033007ar>

#### Résumé de l'article

Six ensembles travertineux de sources chaudes et deux ensembles à température ambiante ont été échantillonnés afin de déterminer les liens entre la teneur en isotopes stables des travertins et celle des eaux dans lesquels ils ont été déposés. Cette analyse a été faite dans le but d'évaluer l'utilité des analyses géochimiques d'anciens travertins pour déterminer la composition des eaux où a eu lieu la précipitation, les conditions climatiques lors de leur formation, etc. Les eaux ont montré une augmentation vers l'aval des valeurs de  $\delta^{13}\text{C}$  dans les huit ensembles et de celles de  $\delta^{18}\text{O}$  dans les six ensembles "chauds". Là où les valeurs des isotopes stables des précipités minéraux montraient parfois des tendances similaires, l'ampleur des changements vers l'aval était habituellement fort différente de celle qu'indiquent les données sur les eaux. De plus, les différents types de précipités, situés à des distances centimétriques les uns des autres, avaient souvent des teneurs isotopiques différentes; ainsi les croûtes formées à l'interface de l'eau et de l'air avaient toujours des valeurs plus élevées de  $\delta^{13}\text{C}$  et de  $\delta^{18}\text{O}$  que les constituants formés à l'intérieur de la colonne d'eau sous-jacente. L'absence d'une relation simple entre la teneur isotopique de l'eau et du précipité est attribuable au fait que la teneur isotopique des précipités est déterminée par un certain nombre de variables, notamment la composition de l'eau, la température, le niveau de saturation, etc. Ces variables peuvent être fort différentes sur de très courtes distances ou au même endroit sur un court laps de temps. Ainsi, comme le démontrent les données sur les isotopes stables, il est fort risqué de vouloir interpréter la composition de l'eau à partir de celle du dépôt.

# STABLE ISOTOPIC VARIABILITY WITHIN MODERN TRAVERTINES

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**ABSTRACT** Six hot and two ambient water travertine systems were sampled to determine the relationships between the stable isotopic composition of the travertines and the waters from which they were deposited. This was conducted in order to evaluate the use of geochemical analyses of ancient travertines for the interpretation of the composition of the waters from which they precipitated, climatic conditions at time of formation, etc. The waters displayed downflow trends of progressively higher (i)  $\delta^{13}\text{C}$  values, in all 8 systems, and (ii)  $\delta^{18}\text{O}$  values, in all 6 hot water systems. Whereas the stable isotopic values of the mineral precipitates sometimes showed similar trends, the magnitude of the downflow changes commonly was quite different than that exhibited by the water data. Additionally, different types of precipitates, which formed within centimeters of each other, commonly had different stable isotopic compositions, e.g., crusts which formed at the air/water interface always had higher  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values than constituents which formed within the immediately subjacent water column. The lack of a simple relationship between stable isotopic composition of the water and the precipitate is due to the fact that the stable isotopic composition of the precipitates are controlled by a number of variables, including the water's composition, temperature, level of saturation, etc. And these variables can change dramatically within very short distances and at the same spot within very short time intervals. Thus, as demonstrated by the stable isotope data, attempting to interpret the composition of the water from the composition of the deposit is a highly risky venture.

**RÉSUMÉ** La variabilité spatiale des teneurs isotopiques à l'intérieur des travertins modernes. Six ensembles travertineux de sources chaudes et deux ensembles à température ambiante ont été échantillonnés afin de déterminer les liens entre la teneur en isotopes stables des travertins et celle des eaux dans lesquels ils ont été déposés. Cette analyse a été faite dans le but d'évaluer l'utilité des analyses géochimiques d'anciens travertins pour déterminer la composition des eaux où a eu lieu la précipitation, les conditions climatiques lors de leur formation, etc. Les eaux ont montré une augmentation vers l'aval des valeurs de  $\delta^{13}\text{C}$  dans les huit ensembles et de celles de  $\delta^{18}\text{O}$  dans les six ensembles « chauds ». Là où les valeurs des isotopes stables des précipités minéraux montraient parfois des tendances similaires, l'ampleur des changements vers l'aval était habituellement fort différente de celle qu'indiquent les données sur les eaux. De plus, les différents types de précipités, situés à des distances centimétriques les uns des autres, avaient souvent des teneurs isotopiques différentes; ainsi les croûtes formées à l'interface de l'eau et de l'air avaient toujours des valeurs plus élevées de  $\delta^{13}\text{C}$  et de  $\delta^{18}\text{O}$  que les constituants formés à l'intérieur de la colonne d'eau sous-jacente. L'absence d'une relation simple entre la teneur isotopique de l'eau et du précipité est attribuable au fait que la teneur isotopique des précipités est déterminée par un certain nombre de variables, notamment la composition de l'eau, la température, le niveau de saturation, etc. Ces variables peuvent être fort différentes sur de très courtes distances ou au même endroit sur un court laps de temps. Ainsi, comme le démontrent les données sur les isotopes stables, il est fort risqué de vouloir interpréter la composition de l'eau à partir de celle du dépôt.

**ZUSAMMENFASSUNG** Dauerhafte isotopische Variabilität innerhalb der modernen Travertine. Sechs Travertin-Systemen mit heißem Wasser und zwei mit der Umgebung angepaßter Wasserwärme wurden Stichproben entnommen, um die Beziehungen zwischen der stabilen isotopischen Zusammensetzung der Travertine und den Quellen, durch die sie abgesetzt wurden, zu bestimmen. Diese Analyse wurde mit dem Ziel durchgeführt, den Nutzen geochemischer Analysen von alten Travertinen bei der Interpretation der Zusammensetzung der Quellen, aus denen sie ausgeschieden wurden, der klimatischen Bedingungen zur Zeit ihrer Bildung u.s.w. zu beurteilen. Die Wasser zeigten talwärts Trends von zunehmend höheren  $\delta^{13}\text{C}$ -Werten in allen 8 Systemen und  $\delta^{18}\text{O}$ -Werte in allen 6 Heißwasser-Systemen. Während die stabilen isotopischen Werte der Mineral-Ausscheidungen manchmal ähnliche Trends zeigten, war der Umfang der Veränderungen talwärts im allgemeinen sehr verschieden von denen, die in den Wasser-Daten angezeigt wurden. Außerdem hatten verschiedene Arten von Ausscheidungen, welche sich in Zentimeter-Entfernung voneinander bildeten, gewöhnlich unterschiedliche stabile isotopische Zusammensetzungen, d.h. Krusten, die sich an der Schnittstelle Luft/Wasser bildeten, hatten immer höhere  $\delta^{13}\text{C}$ - und  $\delta^{18}\text{O}$ -Werte als Bestandteile, welche sich innerhalb der direkt darunterliegenden Wasser-Säule bildeten. Das Fehlen einer einfachen Beziehung zwischen stabiler isotopischer Zusammensetzung des Wassers und der Ausscheidung beruht auf der Tatsache, daß die stabile isotopische Zusammensetzung der Ausscheidungen durch eine Reihe von Variablen kontrolliert werden wie Zusammensetzung des Wassers, Temperatur, Saturations-niveau u.s.w. Und diese Variablen können sich dramatisch verändern innerhalb sehr geringer Entfernungen und an derselben Stelle innerhalb sehr kurzer Zeiträume. Wie die stabilen isotopischen Daten zeigen, ist also der Versuch, die Wasserzusammensetzung von der Zusammensetzung der Ablagerung aus zu interpretieren ein, hoch riskantes Unternehmen.

## INTRODUCTION

Travertines, although rarely recognized in pre-Pleistocene age strata (Kottlowksi, 1953; Steinen *et al.*, 1987), are fairly common among Quaternary age deposits (Feth and Barnes, 1979; Ford, 1989; Pedley, 1990). These modern travertines (sometimes referred to as tufas, calcareous sinter, Mexican onyx, onyx marble, etc.) have been the subject of some intensive geochemical analyses in recent years in order to determine the chemistry of the waters from which they precipitated, geothermal conditions, paleoclimatic conditions, etc. (Cortesi and Leoni, 1955; White *et al.*, 1975; Manfra *et al.*, 1976; Barbieri *et al.*, 1979; Hennig *et al.*, 1983; Goff and Shevenell, 1987; Lao and Benson, 1988; Kronfeld *et al.*, 1988; Pazdur *et al.*, 1988; Szabo, 1990). However, it is essential that the processes involved in the deposition of travertine be fully understood before elemental and isotopic abundances of ancient deposits are used to interpret the conditions at the time of formation.

Travertine deposition is the result of abiotic, biotic, and biotically induced precipitation of calcium carbonate from spring-fed waters (Barnes, 1965; Golubic, 1969; Chafetz and Folk, 1984; Folk *et al.*, 1985; Pentecost and Spiro, 1990; Chafetz *et al.*, 1991a; Folk, 1993). These waters commonly are highly charged in CO<sub>2</sub> and the waters degas with flow away from the spring orifice. As a result of the degassing, the waters generally become highly supersaturated with respect to calcium carbonate and precipitation of solid calcium carbonate occurs, most commonly calcite and aragonite. It is the goal of this paper to demonstrate, with the presentation of stable isotopic data, that travertine systems have a highly dynamic nature. As a consequence of the highly dynamic nature of these systems, modern travertines at the time of deposition display large scale variations in their chemical make-up within laterally adjacent, temporally equivalent precipitates, and thus, sampling and interpretation of geochemical data from ancient travertines must be done with extreme care.

## FIELD LOCATION

In order to evaluate the spatial changes within travertine systems, the waters, and the precipitates that formed from these waters, were analyzed from a number of sites of actively precipitating travertine. Data were gathered from travertine systems at: (i) Mammoth Hot Springs, Yellowstone National Park, Wyoming, U.S.A., (ii) north of Durango, Colorado, U.S.A., (iii) Pagosa Springs, Colorado, U.S.A., (iv) Honey Creek and Falls Creek, Arbuckle Mountains, Oklahoma, U.S.A., (v) Bridgeport, California, U.S.A., (Fig. 1), and (vi) two sites in the vicinity of Viterbo, Italy. The deposits in the Arbuckle Mountains (iv) are part of ambient temperature systems whereas all of the others are hot water systems, *i.e.*, the term hot water system is used for any in which the temperature of the water is elevated above that of the ground-water for that region.

Mammoth Hot Springs is a terraced mound travertine deposit, approximately 75 m thick, all of which is Holocene in age (Weed, 1888; Allen and Day, 1935; White *et al.*, 1975;

Bargar, 1978; Chafetz and Folk, 1984; Pursell, 1985; Sturchio, 1990; Farmer and DesMarais, 1992). This present investigation focused exclusively on the waters and precipitates associated with Narrow Gauge Springs at Mammoth Hot Springs. These springs are situated on Narrow Gauge Terrace, along the upper Terrace Loop Road, at an elevation of approximately 2,000 m above sea level (Fig. 2). Narrow Gauge was the most extensively sampled travertine system during the course of this investigation. The waters and the travertine actively precipitating at this site were sampled during the summers of 1990 and 1991.

The site north of Durango, Colorado (Fig. 3), was first sampled during the summer of 1988 (Chafetz *et al.*, 1991a) and additional sampling was conducted during the summer of 1990. For relevant field relationships, etc., see Chafetz *et al.* (1991a). The Pagosa Springs travertine site lies just south of the center of Pagosa Springs (Fig. 3); a reconnaissance sampling of this system was carried out during the same two trips that were made to study the travertine near Durango.

Active travertine precipitating streams (Honey Creek and Falls Creek) and their associated deposits (*e.g.*, Turner Falls) in the Arbuckle Mountains of Oklahoma (Fig. 4) were extensively sampled as part of theses (Love, 1985; Utech, 1988). For details concerning this overall accumulation see Emig (1917), Love and Chafetz (1988, 1990), and Chafetz *et al.* (1991b).

Reconnaissance sampling was also conducted approximately 3 km south of Bridgeport, California, along a travertine fissure ridge (Fig. 5) during the summer of 1992. For a detailed map, geologic relationships, gross morphology of the travertine accumulation, etc., see Chesterman and Kleinhampl (1991). Two active spring sites in the vicinity of Viterbo, Italy, Le Zitelle (Fig. 6) and Bagnaccio, were also



FIGURE 1. Map showing the location of the travertine sites in the U.S. which are discussed in text, including Y = Mammoth Hot Springs, Yellowstone National Park, Wyoming; D = Durango, Colorado; P = Pagosa Springs, Colorado; B = Bridgeport, California; T = Honey Creek and Falls Creek, Oklahoma.

Carte de localisation des sites de travertine aux États-Unis dont on parle dans le texte: Y = Mammoth Hot Springs, parc national Yellowstone, Wyoming; D = Durango, Colorado; P = Pagosa Springs, Colorado; B = Bridgeport, Californie; T = Honey Creek et Falls Creek, Oklahoma.

sampled during the summer of 1992. For a more detailed overall description of the Viterbo sites the reader is referred to Folk (1994).

## METHODS

### FIELD

The number and type of analyses varied from site to site, the majority of the data were gathered over a five year period, from 1987 through 1992. In general, the data consisted of: (i) water chemistry ( $^{\circ}\text{C}$ , pH, titration for bicarbonate concentration, and elemental and stable isotopic composition), and (ii) petrography and geochemistry of (a) natural precipitates, as well as, (b) precipitates which formed on artificial substrates placed in the water. Where feasible, the water data and water samples were collected from the springs as well as downflow sites. Additionally, mineral precipitates were col-

lected along the flow path. Thus, downflow changes in the chemistry of the waters and precipitates could be analyzed for and evaluated. Precipitate and water sample "pairs" were collected at a number of sites, that is, *in situ* water data and water and mineral samples were collected as closely to the same spot as possible, *i.e.*, within centimeters of each other where feasible.

The temperature and pH were measured *in situ* using Corning 107 and 108 pH/temperature probes. Probes were calibrated prior to use with pH 7 and pH 10 buffers and are accurate to  $0.4^{\circ}\text{C}$ , whereas the pH has a standard deviation of 0.01. Water samples were collected at the sites for bicarbonate, elemental, and oxygen and carbon isotopic analyses. The water sample containers were thoroughly cleaned in the laboratory and then rinsed in the spring water and, wherever possible, sealed while still under water to avoid any contact with the atmosphere. Bicarbonate concentrations were

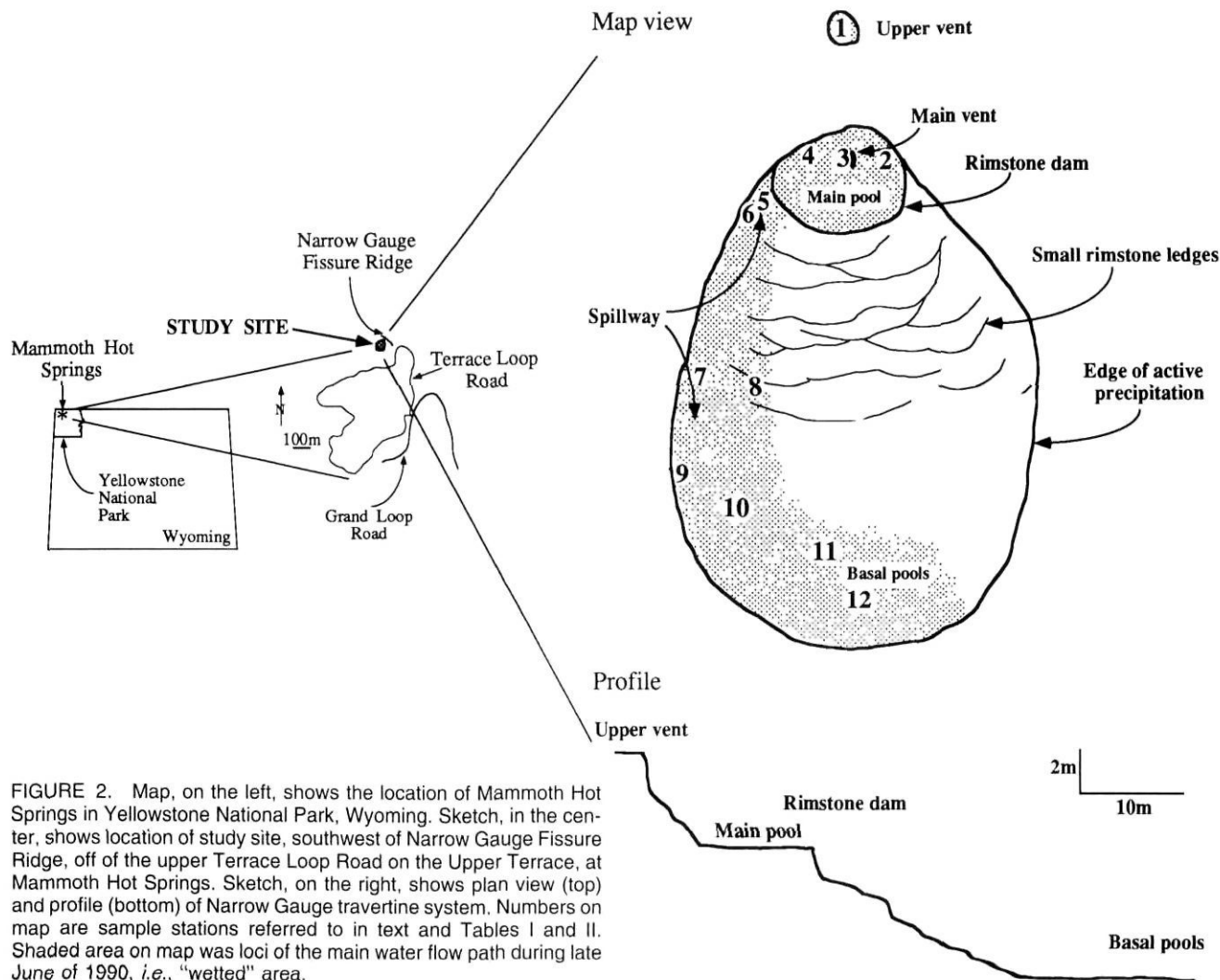


FIGURE 2. Map, on the left, shows the location of Mammoth Hot Springs in Yellowstone National Park, Wyoming. Sketch, in the center, shows location of study site, southwest of Narrow Gauge Fissure Ridge, off of the upper Terrace Loop Road on the Upper Terrace, at Mammoth Hot Springs. Sketch, on the right, shows plan view (top) and profile (bottom) of Narrow Gauge travertine system. Numbers on map are sample stations referred to in text and Tables I and II. Shaded area on map was loci of the main water flow path during late June of 1990, *i.e.*, "wetted" area.

À gauche, carte de localisation des Mammoth Hot Springs, au parc national de Yellowstone, au Wyoming. Au centre, le tracé montre la localisation du site à l'étude, dans le sud-ouest du Narrow Gauge Fissure Ridge, à l'écart de la Terrace Loop Road, à Mammoth Hot Springs. À droite, le schéma montre en plan et en profil l'ensemble travertineux de Narrow Gauge. Les chiffres représentent des sites d'échantillonnage dont on parle dans le texte et dont font référence les tableaux I et II. La zone trannée représente le lieu de passage de l'écoulement principal à la fin juin 1990.



determined in the early phase of this study by titration to the methyl orange end-point and later by titration monitored by the pH meter. During the early phase of the investigation, waters for elemental analyses were collected in tightly sealable glass containers and refrigerated in order to inhibit both abiotic precipitation as well as biologic growth before transportation back to the laboratory for analyses. For the majority of the analyses, the waters were filtered through a 4  $\mu\text{m}$  millipore filter and acidified before refrigeration and transportation back to the laboratory in tightly sealed glass containers for analyses. No recognizable differences were observed in the compositional data between the (i) non-filtered and non-acidified, and (ii) filtered and acidified analyses from resampled systems, thus the data are comparable. Waters for stable isotopic analyses were collected in 16 ml flint glass bottles with poly-seal tops. One drop of mercuric chloride was added to each sample for carbon isotopic analyses to kill any microscopic organism which could alter the carbon isotopic signature.

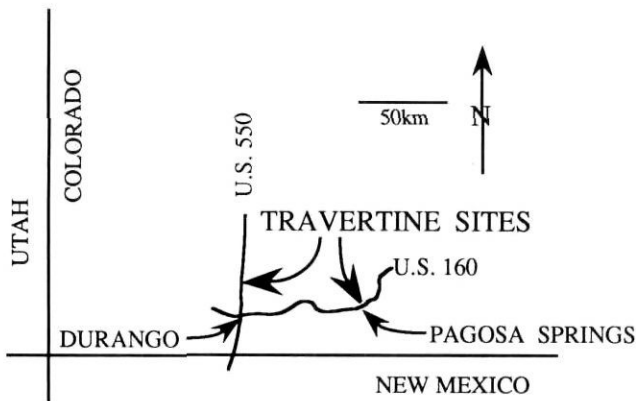


FIGURE 3. Map showing relative locations of Durango and Pagosa springs in southwestern Colorado. For detailed description and sketch map of travertine accumulation of the Durango system see Chafetz *et al.* (1991a).

Carte montrant la localisation du Durango Springs et du Pagosa Springs, dans le sud-ouest du Colorado. Chafetz *et al.* (1991) donnent une description détaillée et une carte des accumulations travertineuses de Durango.

Natural precipitates of calcite and aragonite were collected from all of the sites. These precipitates ranged from well-lithified old (predominantly Holocene) travertine to diaphanous, floating crusts which precipitated within minutes prior to collection. In addition, artificial substrates, predominantly rectangular pieces of a copper sheet, were placed on the sediment/water interface and collected, generally within four days, along with the precipitates that had formed on them. Copper was used because of its general toxicity to algae (Huntsman and Sunda, 1980), and therefore, the likelihood that the initial precipitate would be abiotic in origin. Water data and samples were collected periodically while precipitation was taking place on the artificial substrates, thus, water chemistry data were gathered several times during the period of mineral precipitation. A number of carbonate samples were obtained which precipitated on the copper substrates immediately beneath sites of active surface crust formation. The copper substrates were at the sediment/water interface whereas the crusts formed at the water/air interface. Thus, the composition of precipitates that formed during the same time interval and only separated by a few centimeters (the depth of the water) could be compared. At some locales, slabbed pieces of rock were used as the artificial substrate. The natural travertine and the precipitates which formed on the artificial substrates were returned to the laboratory for petrographic, SEM, elemental, and stable isotopic analyses.

#### LABORATORY

Elemental concentrations within water and mineral samples were determined by standard atomic absorption analyses (Perkin-Elmer Atomic Spectroscopy Model 5000). Standard titration methods were used to determine chlorinity. Sulphate and phosphate concentrations were determined by spectrophotometric analyses (Spectronic 20 Spectrophotometer) (Franson, 1976). Mineralogy was determined by X-ray diffraction where sufficient sample was available and by SEM analyses of stained travertine for small samples (see Chafetz *et al.*, 1991a, fig. 4). Oxygen and carbon stable isotopic compositions were evaluated using a Finnigan-MAT Delta E mass spectrometer. For the water samples, carbon isotopes were determined by liberation of  $\text{CO}_2$  in 100%  $\text{H}_3\text{PO}_4$  at room temperature (Miller, 1980) and oxygen

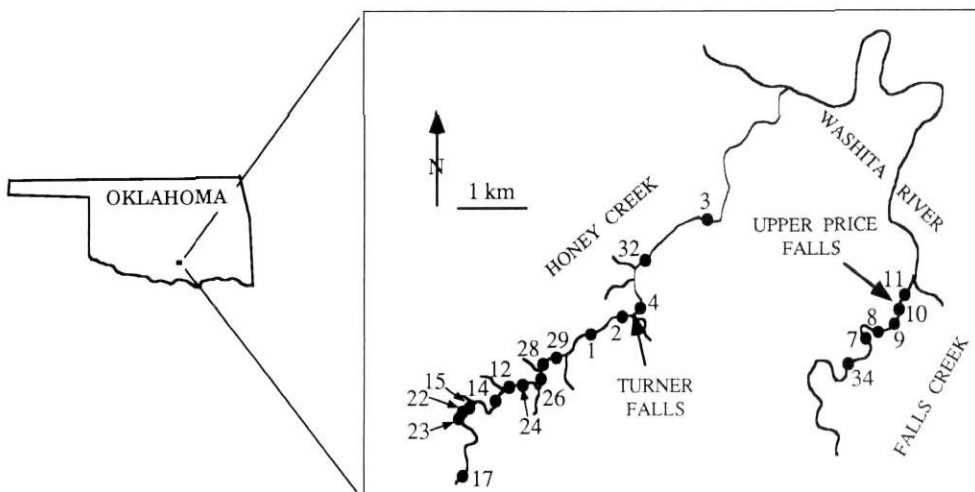


FIGURE 4. Map showing location of Honey Creek and Falls Creek in southcentral Oklahoma and a detailed sketch of the sample stations along those creeks.

Carte de localisation de Honey Creek et de Falls Creek, dans le centre-sud de l'Oklahoma, et de l'emplacement des sites d'échantillonnage.

isotopes were run against tank  $\text{CO}_2$  at  $50^\circ\text{C}$  standardized to NBS-20. Mineral samples were reacted with  $\text{H}_3\text{PO}_4$  at  $50^\circ\text{C}$ . The  $\delta^{18}\text{O}$  values for the waters are given relative to SMOW whereas  $\delta^{18}\text{O}$  values of the minerals and all  $\delta^{13}\text{C}$  values are relative to PDB.

Field and laboratory analyses enabled computation of  $P_{\text{CO}_2}$  and  $I_{\text{SAT}}$  values for the waters by use of computer programs (WATEQ4F and SOLMNEQ.88). Unless otherwise stated, the saturation state of the water (1 equals saturation, 3 equals three times saturation, etc.) is reported relative to aragonite.

In general, the average values for the various analyses will be discussed in the text, e.g., the average pH of the water for a specific sampling station. The average values give the best representation of the overall changes in chemistry and also tend to decrease the apparent significance of any unusual, possibly spurious values. However, it is the authors' belief that individual analyses which have values out of the ordinary can represent the most significant events, i.e., analogous to the thousand year flood.

## RESULTS

### NARROW GAUGE SPRINGS

Narrow Gauge Springs at Mammoth Hot Springs (Wyoming) is a relatively small spring(s) which issued into a

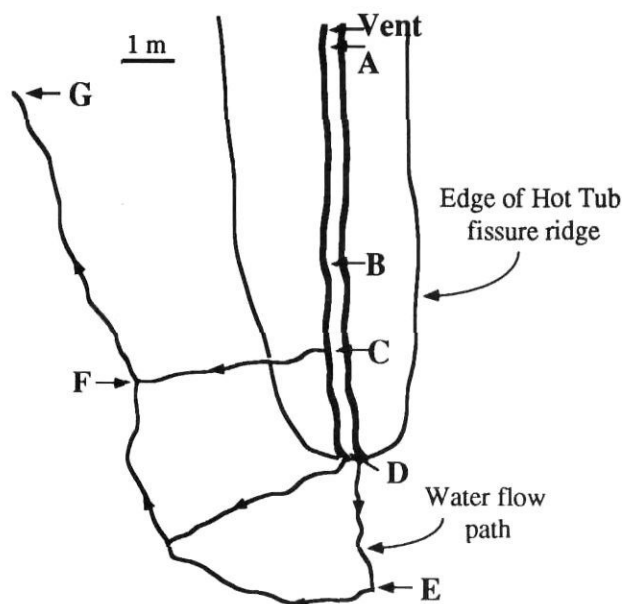


FIGURE 5. Sketch of the southwestern end of Hot Tub Ridge, Bridgeport, California. The spring issues within a fissure and the water flows over the side and southwestern end of the ridge; arrows show direction of water flow. Sample stations are those referred to in Table VII. Detailed maps and color photographs of this system are reproduced in Chesterman and Kleinhampl (1991).

*Schéma de l'extrémité sud-ouest du Hot Tub Ridge, à Bridgeport en Californie. La source s'écoule d'une fissure et l'eau s'écoule sur le flanc et à l'extrémité sud-ouest de la crête. Les flèches donnent la direction de l'écoulement. Les sites d'échantillonnage sont ceux du tableau VII. Chesterman et Kleinhampl (1991) offrent des cartes détaillées et des photographies couleurs de l'ensemble.*

small depression on the southwest side of the Narrow Gauge Fissure Ridge travertine accumulation (see plate 1, Geologic Map in Bargar (1978) for a topographic base map as well as Narrow Gauge's relationships to other springs). The majority of the data were collected in June 1990. The morphology of the overall travertine build-up, spring location, drainage pattern, etc., had changed significantly during the 13 months between the two sampling trips, June 1990 and July 1991. Thus, it was not possible to resample the "same spring", flow pattern, etc.

The springs, during this period, were building a small terraced mound accumulation. Water bubbled in an upper vent (Fig. 2, station 1), about 4 m above the main vent, but this was not connected to the rest of the system by surface flow. Below the upper vent, during the first sampling trip, the water issued from a main vent (Fig. 2, station 3), through a fissure within a pool approximately 10 m in diameter. The pool was surrounded by a rimstone dam and water depth was generally less than 15 cm. Water flowed out over a low point in the rimstone dam and down a "spillway" along the west side of the accumulation to lower levels; water was generally a few centimeters deep along the spillway. At the base of the system, the water was ponded in rimstone dammed pools, water depth was commonly 10 to 20 cm (Fig. 2, stations 11 and 12). The total relief of the active part of the Narrow Gauge terrace mound build-up was approximately 4 m and length of flow before total infiltration, and thus, loss of surface water flow was 50 to 60 m.

### Water Data

A total of 52 suites of water samples (each suite consisted of samples for bicarbonate, elemental,  $\delta^{13}\text{C}$ , and  $\delta^{18}\text{O}$  analyses) were collected along with the *in situ* measurements of  $^\circ\text{C}$  and pH during five sampling periods in June 1990 (Table I). A suite of samples from each station was collected at least three times.

The average values of the water temperature ranged from a high of  $66^\circ\text{C}$ , reaching  $72^\circ\text{C}$  when the probe was held as deeply as possible ( $\sim 10$  cm) within the main vent (station 3), to a low of  $36^\circ$  in the standing pool of water at the base of the flow (station 12) (Table I). The lowest average pH value recorded was for the uppermost vent, 6.27, whereas the main vent averaged 6.45 (stations 1 and 3, respectively) (waters at  $66^\circ\text{C}$  and a pH of approximately 6.45 are neutral (Johnson *et al.*, 1992)). The highest values recorded were at the base of flow, these reached an average pH of 7.67 (station 12). The waters issued from both the upper and the main vents already

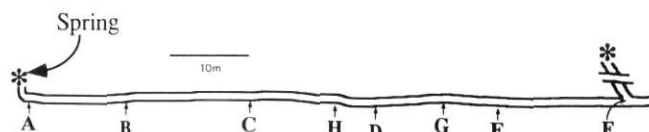


FIGURE 6. Simple sketch shows the relative position of the two springs at Le Zitelle, Viterbo, Italy, and the relative position of the sample stations referred to in Table VIII.

*Schéma montrant l'emplacement des deux sources à Le Zitelle, à Viterbo en Italie, et des sites d'échantillonnage dont fait référence le tableau VIII.*

TABLE I  
Narrow Gauge water data (1990)

	11 am 6/25					7:30 pm 6/25					7:30 am 6/26					3:30 am 6/26					9:30 am 6/27					Average				
	Sta	T <sub>o</sub>	pH	δ <sup>18</sup> O	δ <sup>13</sup> C	T <sub>o</sub>	pH	δ <sup>18</sup> O	δ <sup>13</sup> C	Isat	T <sub>o</sub>	pH	δ <sup>18</sup> O	δ <sup>13</sup> C	Isat	T <sub>o</sub>	pH	δ <sup>18</sup> O	δ <sup>13</sup> C	Isat	T <sub>o</sub>	pH	δ <sup>18</sup> O	δ <sup>13</sup> C	Isat	T <sub>o</sub>	pH	δ <sup>18</sup> O	δ <sup>13</sup> C	
1	69.6	5.70	0.4	-0.53		64.1	6.56	2.8	-0.40	-18.45	65.2	6.40	1.9	-0.34	-18.09	65.5	6.24	1.7	-0.75	-18.20	64.9	6.45	2.6	-0.79	-18.22	65.9	6.27	1.9	-0.56	-18.06
2	46.4	7.02	4.1	0.56		42.3	7.02	4.4	1.36	-17.88	46.9	7.47	14.3	0.61	-17.62	46.2	7.50	12.4	0.56	-17.37	45.5	7.25	8.8	0.77	-17.62	45.5	7.25	8.8	0.77	-17.62
3	55.0	6.10	-0.90			67.3	6.71	4.9	-1.87	-18.31	72.3	6.44	2.7		-17.98	69.2	6.55	3.8	-0.94	-18.17	66.0	6.45	3.8	-1.24	-18.26	66.0	6.45	3.8	-1.24	-18.26
4	40.0	7.26	5.6	1.523		39.2	7.22	5.4	0.41	-18.50	43.4	7.14	5.4	1.06	-17.40	39.2	7.26	5.6	0.18	-17.37	40.5	7.22	5.5	0.79	-17.18	40.5	7.22	5.5	0.79	-17.18
5	66.0	6.79	5.6	-0.24		66.2	6.93	8.8	-0.03	-16.77	65.4	6.93	9.8	0.32	-18.05	66.4	6.87	8.6	-0.37	-18.25	67.0	6.80	4.9	-0.20	-18.07	66.2	6.82	7.5	-0.10	-17.85
6	61.4	7.22	11.0	0.18		55.6	7.68	21.0	0.66	-17.66	55.0	7.63	22.7	0.82	-18.00	54.6	7.60	23.8	0.76	-17.80	54.8	7.60	25.3	0.60	-18.03	55.1	7.60	21.1	0.70	-17.87
7	55.4	7.50	12.6	0.65		55.6	7.68	21.0	0.66	-17.66	55.0	7.63	22.7	0.82	-18.00	54.6	7.60	23.8	0.76	-17.80	54.8	7.60	25.3	0.60	-18.03	55.1	7.60	21.1	0.70	-17.87
8				1.07							52.1	7.70	1.18		-17.67	51.5	7.59		0.53	-17.71					51.8	7.65		0.93	-17.69	
9	48.3	7.51	10.1	1.42							46.8	7.50	10.0	1.41	-17.77	47.6	7.45	9.4	1.31	-17.70	48.2	7.40	9.1		-17.50	47.7	7.47	9.7	1.38	-17.70
10				0.80							44.9	7.69	13.6	1.66	-17.59	45.4	7.56	12.2	1.32	-17.45	42.5	7.57	9.4	2.09	44.3	7.61	11.7	1.47	-17.53	
11	39.3	7.66		2.05							39.3	7.78	13.2	2.05	-17.21	40.6	7.62	11.6	1.88	-17.31	36.9	7.55	6.9	1.77	-17.47	39.0	7.65	10.6	1.94	-17.35
12	36.6	7.56	7.3	2.01		35.6	7.80	11.2	1.56	-17.29	38.5	7.72	10.9	1.90	-17.46	39.1	7.53	9.4	1.76	-18.00	30.7	7.74	7.7	2.34	-17.15	36.1	7.67	9.3	1.91	-17.58

The last data set presents average values of the five data sets.  $\delta^{13}\text{C}$  values are relative to aragonite saturation,  $\delta^{18}\text{O}$  to PDB, and  $\delta^{18}\text{O}$  to SMOW. The dates represent time of collection of data. Station locations are shown on Figure 2.

supersaturated with respect to aragonite and rapidly increased in degree of supersaturation with flow away from the orifice. The saturation index reached a high of approximately 20 in the vicinity of station 7 and then decreased to near 10 at the base of flow (Table I). The increase in the upper part of the system occurred concomitant with precipitation, thus, the relative increase in concentration of the reactants within the water was occurring more rapidly than precipitation was removing them. Obviously, this system is not in equilibrium. The average  $\delta^{18}\text{O}$  values of the water display an increase of less than 1 permil between the vents and the downflow sites (Fig. 7A). The  $\delta^{13}\text{C}$  values of the water, on the other hand, display a large increase downflow, approximately 3.2‰, (-1.24 to 1.94‰ PDB, Table I, Fig. 8A). These changes occur in less than 60 m of flow.

#### Precipitate Data

Three different varieties of naturally occurring samples were collected; these included (i) precipitates on biologic structures (bacteria, algae, etc.), (ii) carbonate-encrusted gas bubbles (see Chafetz *et al.*, 1991a, for a description of this type of allochem), and (iii) crusts (also referred to in the literature as ice, rafts, etc.) which precipitate as a floating layer on the surface of the water. In addition, precipitates which formed on the artificial substrates were also collected. Essentially all of the material collected and analyzed was aragonite or predominantly aragonite. Table II lists the station at which each of the samples was collected, the stable isotopic data from their analyses, and the theoretical  $\delta^{18}\text{O}$  values of aragonite precipitated in equilibrium with the average  $\delta^{18}\text{O}$  composition and temperature of the waters for each sample station. The theoretical  $\delta^{18}\text{O}$  values for calcite are approximately 0.5‰ lower (more negative) than those for aragonite.

The  $\delta^{18}\text{O}$  values of the aragonite for all precipitates displayed an average increase in the downflow direction of around 4.5 permil. This increase was from -24.8‰ PDB at the main vent (station 3) and -25.1‰ at the head of the spillway (station 5) to -20.5‰ at the basal pool (station 12) (Table II). This increase is paralleled by the changes in the  $\delta^{18}\text{O}$  values of the precipitates on the biologic structures, copper substrates, floating crusts, and theoretical precipitates. The  $\delta^{18}\text{O}$  values for the theoretical precipitates are generally the lowest value for any particular station. On the average, successively higher  $\delta^{18}\text{O}$  values are displayed by the biologic structures, carbonate-encrusted gas bubbles and precipitates on copper substrates, and the floating crusts (Fig. 9A). The crusts display the highest measured  $\delta^{18}\text{O}$  values at all but one station.

The  $\delta^{13}\text{C}$  values also display an increase in the downflow direction, however, this is not as pronounced as that displayed by the  $\delta^{18}\text{O}$  values. On the average, the  $\delta^{13}\text{C}$  values increase by 2 permil, from 3.0 at the main vent (station 3) to 5.0‰ PDB at the basal pool (station 12) (Table II). For the individual stations, the precipitate on the copper substrate exhibits the lowest value, followed by increasingly higher values for the biologic structures (although overlap with substrate values occurs), carbonate-encrusted gas bubbles, and the crusts. With one minor exception, the crusts display the highest  $\delta^{13}\text{C}$  values at every station (Table II, Fig. 9B).

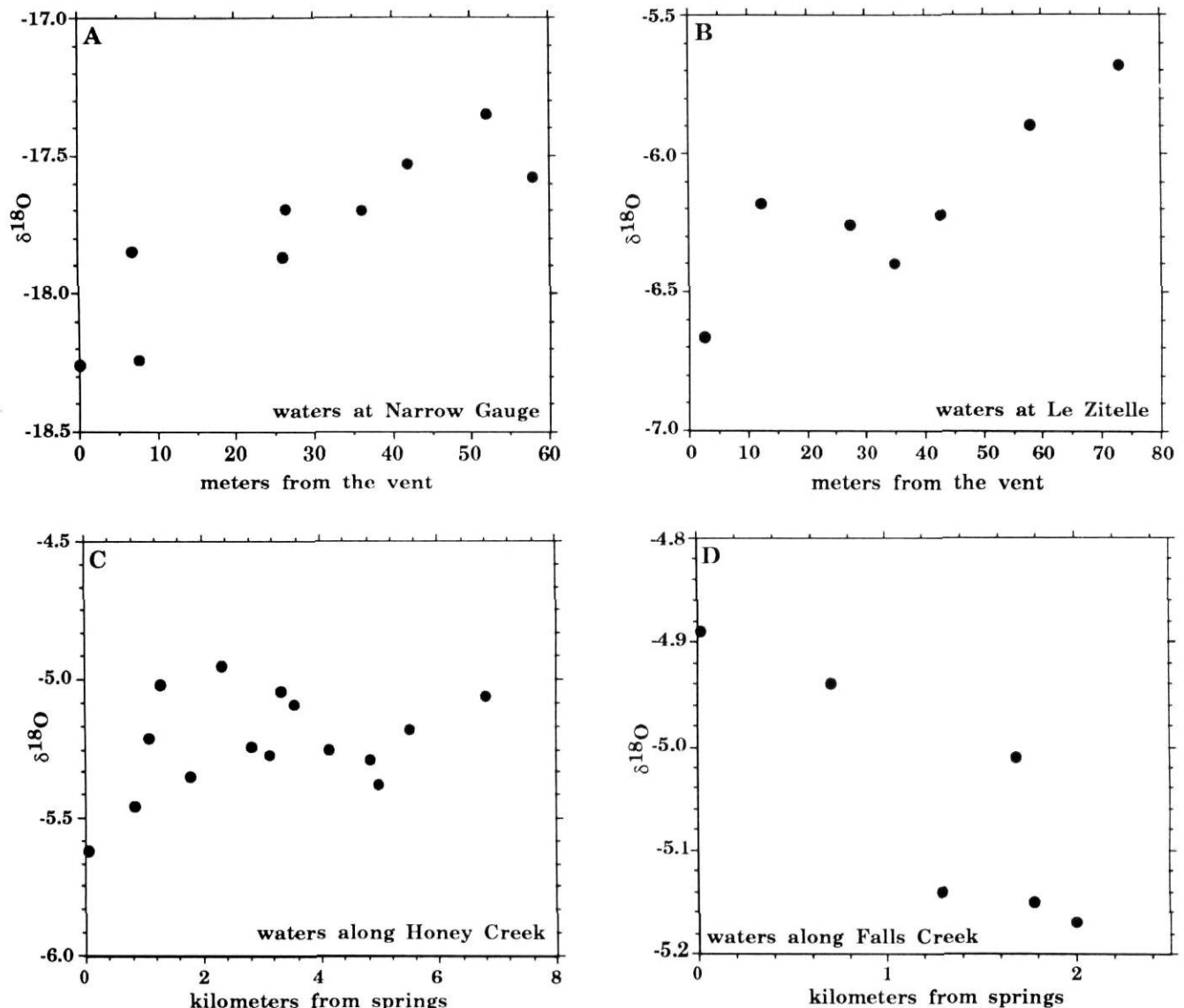


FIGURE 7. Bivariate plots of  $\delta^{18}\text{O}$  values of the waters versus distance downflow for two hot water travertine systems (A and B) and two ambient temperature systems (C and D). Observe the well-developed increase in  $\delta^{18}\text{O}$  values downflow (A and B) which is characteristic of all six hot water systems. The  $\delta^{18}\text{O}$  composition of Honey Creek (C) does not display a discernible trend whereas the composition of Fall Creek (D) displays a slight decrease ( $\sim 0.3\text{‰}$ ) over 2 km.

Graphique des valeurs  $\delta^{18}\text{O}$  des eaux sur la distance en aval de la source de deux ensembles travertineux de sources chaudes (A et B) et de deux ensembles à température ambiante (C et D). Noter la nette augmentation de  $\delta^{18}\text{O}$  vers l'aval (A et B) qui est caractéristique des six ensembles de sources chaudes. La composition  $\delta^{18}\text{O}$  de Honey Creek (C) ne montre pas de tendance notable, tandis que celle de Fall Creek (D) montre une légère diminution de  $\sim 0,3\text{‰}$  sur 2 km.

During the summer of 1991, Narrow Gauge was revisited and a modest sampling program was established to collect additional data on the stable isotopic composition of the water and immediately adjacent precipitates of different origins (*i.e.*, coating on biologic structures, precipitates on copper substrates, and crusts which form at the water/air interface). Seven stations were sampled approximately three days apart. Because of the marked change in the location of the active vents, the drainage patterns, etc., these samples have no detailed relationship to those collected the previous year. For example, the main vent with its associated pool (Fig. 2, stations 2, 3, 4) was completely dry and inactive when visited during July of 1991.

The samples collected during 1991 display the same general trends as those collected during 1990. Similar to the previously attained results for  $\delta^{18}\text{O}$  values at each station, the theoretical precipitates from these waters exhibit the lowest values, followed by increasingly higher values for biologic structures, precipitates on copper substrates, and the crusts, which with one exception have the highest values (Table III, Fig. 9A). The  $\delta^{13}\text{C}$  values of the carbonates on the copper substrates generally are the lowest, but they have considerable overlap with the values of the biologic structures. Similar to the results attained in 1990, the crusts generally display the highest  $\delta^{13}\text{C}$  values (Table III, Fig. 9B).



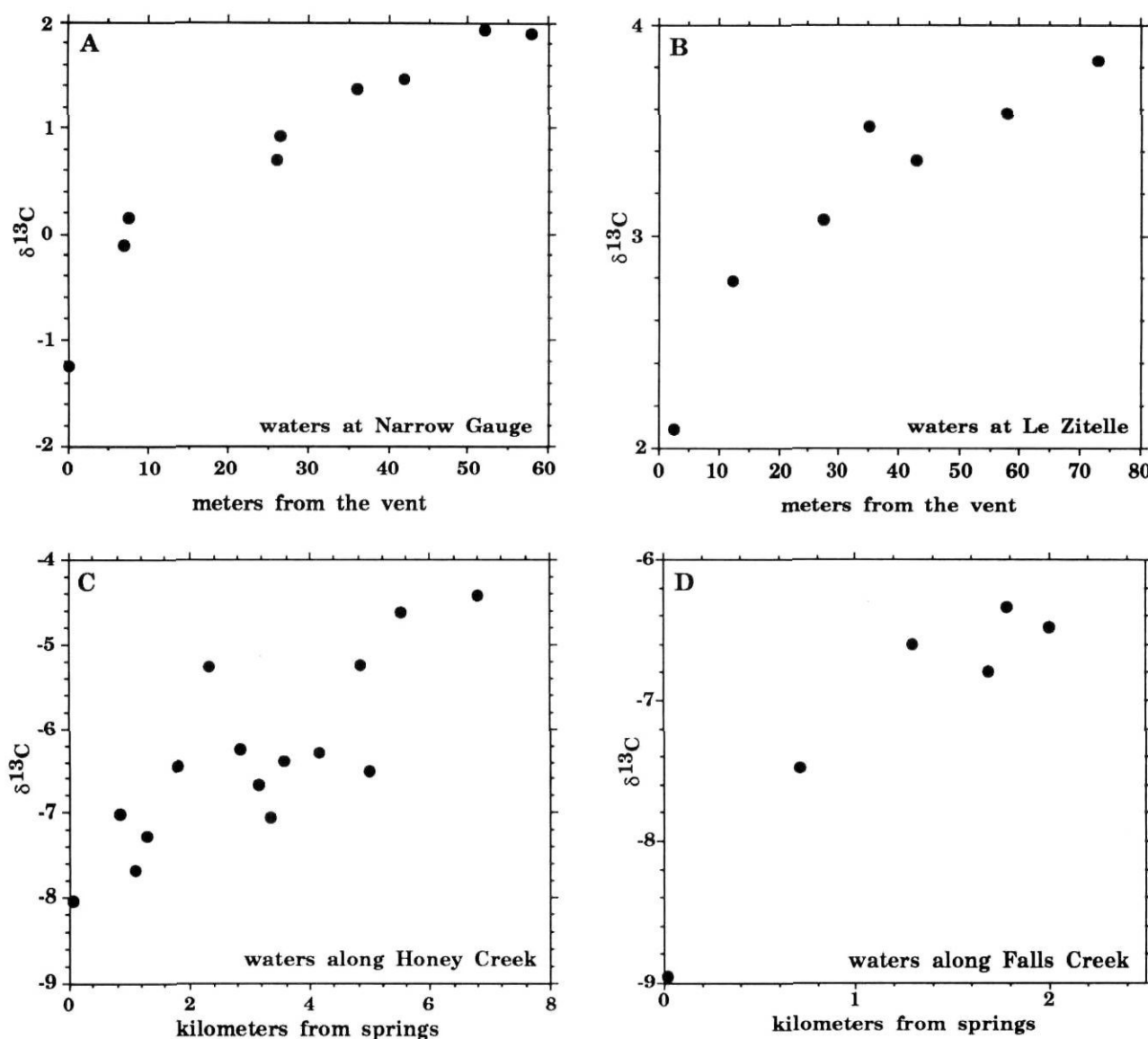


FIGURE 8. Bivariant plots of  $\delta^{13}\text{C}$  values of the waters versus distance downflow for two hot water travertine systems (A and B) and two ambient temperature systems (C and D). Observe the well-developed and relatively large permil increase in  $\delta^{13}\text{C}$  values with distance downflow.

Graphique des valeurs de  $\delta^{13}\text{C}$  des eaux sur la distance en aval de la source de deux ensembles travertineux de sources chaudes et de deux ensembles à température ambiante (C et D). Noter la nette augmentation des valeurs de  $\delta^{13}\text{C}$  avec la distance en aval.

## DURANGO

This hot spring exists along U.S. highway 550 approximately 17 km north of Durango, Colorado, U.S.A. (Fig. 3). This actively precipitating system was described in considerable detail in Chafetz *et al.* (1991a), and thus, the reader is referred to that publication for all relevant background information. The previously reported data were collected in 1988 and this site was resampled using somewhat different techniques (*e.g.*, the waters were millipore filtered and acidified before refrigeration and transported to the laboratory for analyses); the results were essentially identical. The samples collected were composed predominantly of calcite; however, some were composed of aragonite or a mixture of the two minerals.

## Water Data

The water data were collected through a lateral flow of approximately 200 m. The temperature of the spring water at this site only reaches a high in the low 30's, considerably cooler than those at Mammoth Hot Spring. However, the water attains a considerably higher degree of supersaturation with respect to carbonate precipitation than attained by the water at Narrow Gauge, *i.e.*, average  $I_{\text{sat}}$  with respect to calcite for the top of the travertine mound was equal to 46 (50 in 1988) (Table IV; see also Chafetz *et al.*, 1991a, table 1). As demonstrated by the analyses of the samples collected in 1988 (Chafetz *et al.*, 1991a, table 1) and again with these analyses, there is a slight increase in the  $\delta^{18}\text{O}$  values from the spring to the base of flow (approximately 0.25‰ and 0.6‰ for

TABLE II  
Stable isotopic data for precipitates at Narrow Gauge, 1990

Sta	$\delta^{18}\text{O}$					$\delta^{13}\text{C}$				
	Bio	GB	Cu	Crst	Avg	Theor	Bio	GB	Cu	Crst
1						-26.86				
2	-24.06			-21.41	-22.74	-23.31	3.31			4.61
3	-24.91		-24.44	-24.91	-24.79	-27.55	3.37		2.21	3.03
4	-25.18	-24.78		-23.06	-24.02	-22.27	3.01	4.06		4.46
5	-25.42	-25.19	-25.17	-23.89	-25.08	-26.69	3.15	3.38	2.74	4.75
6	-24.98				-24.98	-26.36	3.42			
6a				-23.80						4.21
6b		-23.96		-23.72	-23.84			3.99		4.35
6c			-24.60	-23.25	-23.93				3.53	4.25
7		-24.16	-24.06	-22.92	-23.85	-25.09		3.87	3.77	4.73
8	-23.86		-23.69		-23.78	-24.04	3.89		3.90	
9			-23.40	-22.16	-22.98	-23.75			4.15	5.02
10	-21.99	-21.16	-21.31	-21.07	-21.36	-23.02	4.09	4.49	4.38	4.87
11			-20.77	-20.49	-20.67	-21.92			4.36	5.30
12				-20.54	-20.54	-21.62				4.98

Analyses are for Bio = precipitates on biologic structures, GB = carbonate-encrusted Gas Bubbles, Cu = precipitates on copper substrates, Crst = floating crusts, Avg = average value for analyzed precipitates, Theor = composition of aragonite which should form in isotopic equilibrium with the waters at these sites. The  $\delta^{18}\text{O}$  values are relative to SMOW and  $\delta^{13}\text{C}$  values are relative to PDB.

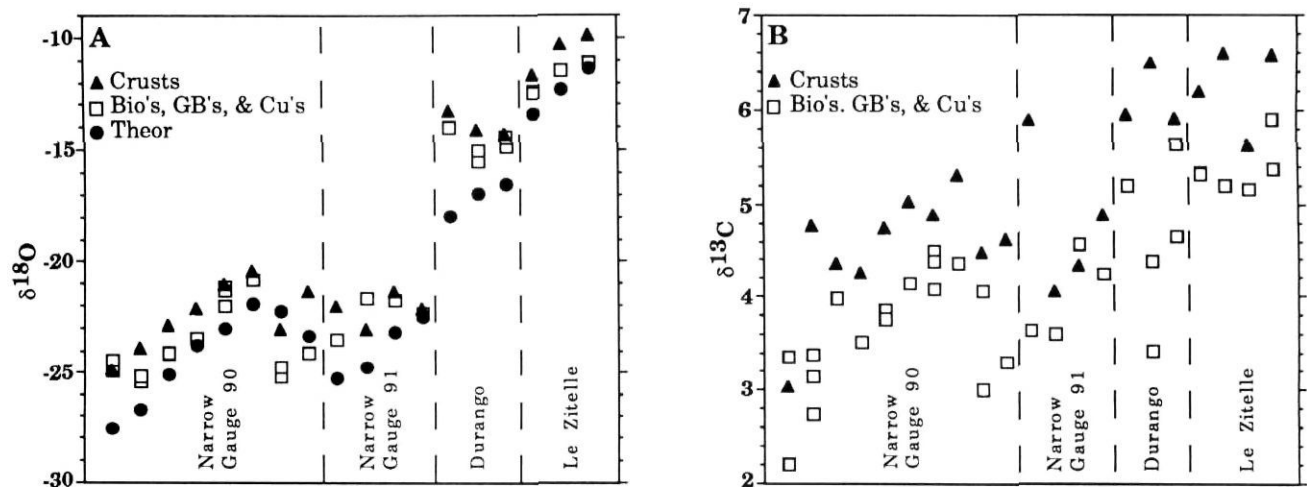


FIGURE 9. Stable isotopic data is grouped by travertine system and plotted for stations near spring orifice (on the left) to downflow stations (on the right). A) Data showing  $\delta^{18}\text{O}$  values for crusts vs precipitates on biologic structures, carbonate-encrusted gas bubbles, and precipitates on copper substrates vs theoretically predicted  $\delta^{18}\text{O}$  values. Only stations for which all three categories of data exist are plotted. Observe that at most stations the theoretical precipitates have the lowest values, the samples that precipitated within the water column have intermediate values, and the crusts have the highest values. B) Data showing  $\delta^{13}\text{C}$  values for crusts vs precipitates on biologic structures, carbonate-encrusted gas bubbles, and precipitates on copper substrates. Observe that at most stations the samples that precipitated within the water column have considerably lower values than the crusts.

Données des teneurs en isotopes stables regroupées par ensemble travertineux et reportées à partir des sites situés près des sources mêmes (à gauche) jusqu'aux sites situés en aval (à droite). A) Valeurs  $\delta^{18}\text{O}$  des encroûtements, par rapport à celles des précipités sur structure biologique, des bulles de gaz encroûtées de carbonate et des précipités sur substrat de cuivre, par rapport aux valeurs théoriques prévues de  $\delta^{18}\text{O}$ . Seuls les sites pour lesquels les trois catégories de données sont disponibles ont été inclus. À la plupart des sites les valeurs théoriques sont les plus basses, dans les échantillons dont la précipitation s'est faite à l'intérieur de la colonne d'eau les valeurs sont intermédiaires et dans les encroûtements les valeurs sont les plus élevées. B) Valeurs  $\delta^{13}\text{C}$  des encroûtements, par rapport à celles des précipités sur structure biologique, des bulles de gaz encroûtées de carbonate et des précipités sur substrat de cuivre. Noter qu'à la plupart des sites, les échantillons dont la précipitation s'est faite à l'intérieur de la colonne d'eau ont des valeurs nettement moins élevées que celles des encroûtements.

TABLE III  
Stable isotopic data for water and precipitates for Narrow Gauge, 1991

Sta	$\delta^{18}\text{O}$							$\delta^{13}\text{C}$			
	T°	H <sub>2</sub> O	Bio	Cu	Crst	Avg	Theor	H <sub>2</sub> O	Bio	Cu	Crst
Vent	77.2	-18.09					-28.36	0.32			
A	74.1	-18.13	-26.83*	-26.36*		-26.60	-28.06	1.45		2.20*	1.81*
B	58.2	-17.58		-23.47*	-22.11	-22.98	-25.27	1.56		3.64*	5.88
C	56.1	-17.73	-24.62*	-24.55		-24.60	-25.07	1.22	3.32	3.39	
D	55.0	-17.60		-21.61	-23.07	-22.34	-24.81	1.31		3.60	4.05
E	47.4	-17.68		-21.77	-21.39	-21.58	-23.19	2.79		4.58	4.32
F	47.2	-17.60			-22.48	-22.48	-23.57	2.35			6.30
G	43.5	-17.67		-22.33	-22.17	-22.25	-22.53	2.32		4.25	4.88

See Table II for the meaning of the abbreviations. The temperature and stable isotopic values of the water represent an average of two readings each as do the asterisked values of the precipitates.

TABLE IV  
Water and precipitate data for travertine system near Durango, Colorado, 1990

Stations		Water Data					Precipitate Data								
		Dist	T °	pH	I <sub>sat</sub>	δ <sup>18</sup> O	δ <sup>13</sup> C	δ <sup>18</sup> O				δ <sup>13</sup> C			
Bio	GB							Crst	Avg	Theor	Bio	GB	Crst	Avg	
Spring	0	32.8	6.11	1.6	-14.26	-2.27									
near sp	2	31.4	6.50	3.9	-14.19	-0.49	-13.99		-13.29	-13.64	-17.96	5.19		5.94	5.57
D-50 m	40	29.9	7.04	15.5	-14.23	0.57									
D-100 m	100	29.0	7.32	20.0	-14.23	0.97									
Md top	140	26.6	7.91	45.9	-14.10	1.90	-15.48	-15.01	-14.16	-14.88	-16.91	3.42	4.38	6.48	4.76
Base	175	25.3	7.93	35.0	-14.01	4.06	-14.84	-14.41	-14.33	-14.27	-16.53	4.66	5.64	5.90	5.40

Data collection sites are located at the spring, immediately downflow of the spring, in the drainage ditch 50 and 100 m downflow, and at the top and base of the mound (see Chafetz *et al.*, 1991a, Fig. 2 for sketch map). The water data are averages for three suits of samples collected over a two day period. Abbreviations are the same as those used in Table II, Isat values are relative to calcite saturation, distance downflow from vent is in meters.

1990 and 1988 samples, respectively) and a very large increase in  $\delta^{13}\text{C}$  values (approximately 6.3‰ and 8.3‰ for 1990 and 1988 samples, respectively) (Table IV).

#### Precipitate Data

Samples of crust, encrusted biologic structures, and carbonate-encrusted gas bubbles were collected at three sites, (i) near the main spring orifice, (ii) on the mound top, and (iii) near the base of the mound (approximately 2, 140, and 175 m downflow, respectively; see Chafetz *et al.* (1991a), fig. 2 for a sketch map), and analyzed for their stable isotopic composition (Table IV). The theoretical precipitates from these waters exhibit the lowest  $\delta^{18}\text{O}$  values, followed by increasingly higher values for carbonate precipitated on biologic structures, carbonate-encrusted gas bubbles, and the crusts, which always have the highest values (Table IV, Fig. 9a). The  $\delta^{13}\text{C}$  values of the carbonate on the biologic structures are the lowest and are succeeded by higher values on the carbonate-encrusted gas bubbles. The crusts always display the highest  $\delta^{13}\text{C}$  values (Table IV, Fig. 9B).

#### PAGOSA SPRINGS

The site within the town of Pagosa Springs (Colorado) is a broad flat area of travertine, in excess of 80 m in diameter, covered by a layer of spring-fed water commonly less than 3 cm deep. The spring-fed water spreads out over the surface and is separated into very shallow pools by an anastomosing network of rimstone dams. Water was collected from the main spring and five sites (14, 18, 28, 50, and 80 m) downflow (Table V). Additionally, three samples of precipitate on biologic structures were sampled.

The water at this site becomes very highly supersaturated with respect to aragonite downflow (Table V). Both the  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values of the waters get considerably higher over the course of 80 m (2.9 and 6.4‰, respectively). The aragonite which precipitated on the predominantly bacterial structures, displays considerably higher  $\delta^{18}\text{O}$  values than would aragonite which precipitated in theoretical equilibrium with these waters (Table V).

## HONEY CREEK AND FALLS CREEK

The travertine at this site in Oklahoma was precipitated as part of ambient water systems in the Arbuckle Mountains. The travertine and diagenesis of the travertine was the subject of a thesis (Love, 1985), as was the elemental and stable isotopic composition of the waters and their precipitates (Utech, 1988). The waters of these two streams were sampled five times, at three month intervals, from March 1987 through March 1988.

## Water Data

Water sampling on Honey Creek covered a lateral distance of approximately 6.8 km and 2.0 km on Falls Creek (Fig. 4), considerably longer distances than within the hot water systems. Stable isotopic analyses of 139 water samples (Chafetz *et al.*, 1991b, table 2) show that the average  $\delta^{18}\text{O}$  values do not display any trend in the downstream direction on Honey Creek but do display a slight decrease (approximately 0.3‰) over 2 km on Falls Creek (Fig. 7c, d). The average  $\delta^{13}\text{C}$  values, on the other hand, display an increase in the downflow direction along both Honey Creek and Falls Creek (3.6 and 2.5‰, respectively, Table VI, Fig. 8C, D).

## Precipitate Data

All of the samples were composed of calcite. Neither floating crusts nor carbonate-encrusted gas bubbles were observed within this system. Artificial substrates composed mainly of slabbed rock were placed in the water for three month periods and the stable isotopic compositions of the precipitates were compared to the theoretically expected calcite precipitates. The artificial substrates were covered with precipitates on biologic structures. Although the data displayed considerable overlap, the precipitates displayed a higher average  $\delta^{18}\text{O}$  value than expected from the calculations based on equilibrium fractionation considerations of the water data (Chafetz *et al.*, 1991b, table 6).

## BRIDGEPORT

This site, in the Sierra Nevada Range of eastern California, was visited briefly during the summer of 1992; parts of it are used as a (nude) bathing site and because of possible contamination with soaps, oils, etc., was not used for data collection. A spring along the crest of Hot Tub Ridge (Chesterman and Kleinhampl, 1991, fig. 3), a fissure ridge, was sampled along with older travertine. The fissure is on the order of 10 cm wide and the water was generally less than 5 cm deep.

The  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values of the water increase approximately 0.9‰ and 1.5‰, respectively, from the vicinity of the spring to a station approximately 15 m downflow (Fig. 5, Table VII). The travertine precipitated along this flow path displayed  $\delta^{18}\text{O}$  values which increased downflow by approximately 3.6‰ whereas the  $\delta^{13}\text{C}$  values got slightly lower downflow. The theoretical travertine, which should have precipitated in equilibrium with these waters, has lower  $\delta^{18}\text{O}$  values at each site than the measured values (Table VII).

TABLE V

*Pagosa Springs water and precipitate data for 1988 and 1990*

Sta	Water Data					Precipitate Data		
	T°	pH	I <sub>sat</sub>	$\delta^{18}\text{O}$	$\delta^{13}\text{C}$	Theor	$\delta^{18}\text{O}$	$\delta^{13}\text{C}$
Vent	53.8	6.37	0.4	-12.66	-3.66	-19.73	-16.77	0.53
14 m	52.7	6.49	1.8	-12.64	-3.39	-19.53	-15.58	0.71
18 m	42.4	7.66	12.5	-12.50	-1.38	-17.69	-16.34	1.21
28 m	37.5	7.87	30.5	-11.50	-0.73		-15.83	
50 m	28.7	8.45	42.3	-12.09	0.74	-14.74		
80 m	34.4	8.03		-9.80	2.73	-13.56		

Water data for the vent, 14 m, and 28 m downflow represent averaged data for 1988 and 1990 samples. Abbreviations are the same as those used in Table II.

TABLE VI

*Average stable isotopic water composition for Honey Creek and Falls Creek.*

Honey Creek				Falls Creek			
Sta	Dist	$\delta^{18}\text{O}$	$\delta^{13}\text{C}$	Sta	Dist	$\delta^{18}\text{O}$	$\delta^{13}\text{C}$
17	0.05	-5.62	-8.03	34	0.02	-4.89	-8.95
23	0.85	-5.46	-7.02	7	0.71	-4.94	-7.48
22	1.08	-5.21	-7.68	8	1.29	-5.14	-6.60
15	1.28	-5.02	-7.28	9	1.69	-5.01	-6.80
14	1.80	-5.35	-6.44	10	1.78	-5.15	-6.34
12	2.31	-4.95	-5.27	11	2.00	-5.17	-6.48
24	2.82	-5.24	-6.24				
26	3.13	-5.27	-6.68				
28	3.34	-5.04	-7.06				
29	3.54	-5.09	-6.39				
1	4.13	-5.25	-6.28				
2	4.85	-5.29	-5.24				
4	4.98	-5.38	-6.52				
32	5.52	-5.18	-4.62				
3	6.80	-5.06	-4.43				

Distance in kilometers downflow from springs, see Figure 4 for location of stations, falls, etc., on map. See Table II in Chafetz *et al.* (1991b) for all of the individual data values.

## LE ZITELLE SPRINGS AND BAGNACCIO SPRING

The two spring sites in the vicinity of Viterbo, Italy, were sampled in May of 1992. Folk (1994, fig. 1) presents a map showing the regional location of these springs plus a general description of the area.

## Water Data

The two springs at Le Zitelle were enclosed within fence-topped stone walls. Thus, the first data collection point is situated after the water flowed over the stone wall, about 1 m high, and down into a straight channel, approximately 2.5 m from where the water actually reached the surface (Fig. 6, station A). The water was sampled through approximately 75 m of lateral flow in a channel that ranged from 1 to 2 m wide and 10's of centimeters to almost a meter deep. The water from the second spring was not sampled.



The  $\delta^{18}\text{O}$  values of the water increase downflow by about 1‰ (Fig. 6, station A to F, Table VIII A, Fig. 7B) whereas the  $\delta^{13}\text{C}$  values increase by 1.7‰ (Table VIIIA, Fig. 8B).

#### Precipitate Data

The calculated theoretical  $\delta^{18}\text{O}$  values for aragonite which should have precipitated out of this water are lower at all stations (with one exception) than the natural precipitates on biologic structures, crusts, and precipitates on copper substrates (Table VIIIB). The one exception, station F, is at the confluence of the waters from the two springs (Fig. 5). The temperature reported was measured just before these waters mixed, after mixing the temperature is much higher. Carbonates that precipitate from higher temperature waters will have lower  $\delta^{18}\text{O}$  values. It is very likely that the carbonate analyzed from this site precipitated in hotter waters. Folk (1994) also noted that 11 days after the 35.5°C measurement was taken, he visited this site again and recorded a temperature of 55°C for this station using the same instrument. A water temperature of 41°C would have resulted in lower calculated  $\delta^{18}\text{O}$  values of the theoretical precipitates than the measured precipitates. Thus, as reported for the other travertine systems, the calculated theoretical  $\delta^{18}\text{O}$  values are lower than the measured values.

Some of the travertine at Le Zitelle is a mixture of aragonite (75%) and calcite (25%), as discussed by Folk (1994). According to equilibrium fractionation considerations, calcite has lower  $\delta^{18}\text{O}$  values than aragonite if precipitated under the same conditions. Thus, if the calculations for the theoretical precipitates were made using the fractionation values for calcite, then the difference in  $\delta^{18}\text{O}$  values between the theoretical precipitates and the natural precipitates would be even greater than those reported.

The natural precipitates, mostly on biologic structures, and those precipitates on copper substrates have similar  $\delta^{18}\text{O}$  values (Table VIIIB). And, as recognized in the data from the other travertine systems, the crusts which precipitate on the surface of the water have the highest  $\delta^{18}\text{O}$  values. The  $\delta^{13}\text{C}$  values of the natural precipitates and those on the copper substrates are approximately equal and, as reported above for the other travertine systems, the crusts always have the highest  $\delta^{13}\text{C}$  values (Table VIIIB, Fig. 9B).

Bagnaccio Spring (Folk, 1994, fig. 1) was also sampled, however, the data from this locale are not of the purest quality. The water issued from a spring and flowed across a dirt road which was heavily traveled by cars bringing local townspeople to inhale the  $\text{H}_2\text{S}$ -rich fumes, drink, and bath in the waters. Thus, lots of detritus was stirred regularly into the spring water. Nevertheless, the same general trends were found in these data as from the other systems. The  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values of the waters increase downflow. The  $\delta^{18}\text{O}$  values of theoretically precipitated carbonate always displays the lowest values and the crusts which formed on the surface of the water always display the highest  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values.

## DISCUSSION

The data from six hot water (Narrow Gauge, Durango, Pagosa Springs, Bridgeport, Le Zitelle, and Bagnaccio) and

TABLE VII

*Stable isotopic values for water and precipitate samples from Bridgeport, California, site*

Sta	Water Data				Precipitate Data		
	T°	pH	$\delta^{18}\text{O}$	$\delta^{13}\text{C}$	Theor	$\delta^{18}\text{O}$	$\delta^{13}\text{C}$
Vent	66.2	6.60	-16.73	-3.22	-25.29	-23.24	-0.47
A	64.0	6.74	-16.77	-3.03	-25.31		
B	63.8	6.85	-16.45	-3.01	-24.97		
C	59.8	7.16	-16.45	-2.87	-24.39		
D	43.1	8.14	-15.91	-1.92	-21.20		
E	46.9	8.08	-15.94	-1.81	-21.87	-20.45	-1.10
F	40.4	8.24	-15.80	-1.69	-20.62	-19.60	-0.68

See Figure 5 for location of individual samples and Table II for meaning of abbreviations.

TABLE VIII

*Water (a) and precipitate (b) data for spring at Le Zitelle, Viterbo, Italy*

A

Sta	Dist	T°	pH	δ <sup>18</sup> O	δ <sup>13</sup> C
Vent		61.0	6.28		
A	2.5	59.0	6.74	-6.66	2.09
B	12.2	54.4	7.39	-6.18	2.79
C	27.4	51.2	7.56	-6.26	3.08
H	35.1	49.0	7.62	-6.40	3.52
D	42.7	47.5	7.62	-6.22	3.47
G	47.2	34.4	7.76		
E	57.9	43.6	7.80	-5.90	3.58
F	73.2	35.3	8.05	-5.68	3.83

B

Sta	δ <sup>18</sup> O				δ <sup>13</sup> C		
	Bio	Cu	Crst	Theor	Bio	Cu	Crst
A	-13.04*			-14.57	4.89*		
B	-12.37	-12.48	-11.66	-13.39	5.33	5.31	6.18
C		-11.47		-12.96		4.93	
H	-11.76	-11.64		-12.74	5.31	5.05	
D		-11.45	-10.35	-12.32		5.19	6.58
G		-10.87	-10.87			5.16	5.62
E	-11.11	-11.12	-9.93	-11.34	5.89	5.38	6.55
F	-10.65*	-10.60		-9.66	5.69*	6.03	

Distance in meters downflow from spring, abbreviations as used in Table II, and see Figure 6 for location of stations. Asterisked values represent an average of two readings.

two ambient (Honey Creek and Falls Creek) travertine systems show some similar trends. The  $\delta^{13}\text{C}$  values of the waters increase downflow in each of the eight systems (e.g., Fig. 8). The  $\delta^{18}\text{O}$  values also increase downflow in the waters of all of the hot water systems investigated. In contrast, the  $\delta^{18}\text{O}$  values in Falls Creek display a small gradual decrease downflow whereas Honey Creek does not exhibit a discernible downflow trend (Fig. 7). In the six hot water systems, the  $\delta^{13}\text{C}$  permil values of the waters display a much greater increase than the  $\delta^{18}\text{O}$  permil values in the downflow

direction. Essentially all precipitates in all eight systems, whether they formed: (i) within the water column on biologic structures, around gas bubbles, or on artificial substrates, or (ii) at the surface of the water (*i.e.*, floating crusts) have  $\delta^{18}\text{O}$  values which are higher than those predicted for that station as determined by calculations using equilibrium fractionation relationships (Fig. 9A). The floating crusts generally display  $\delta^{18}\text{O}$  values which are slightly higher than those precipitates which formed at the same station but within the water column, such as the precipitates on copper substrates and biologic structures. Additionally, the floating crusts almost always have  $\delta^{13}\text{C}$  values which are substantially higher than those of precipitates which formed within the water column at the same station (Fig. 9B). These relationships, which this study has documented for a number of different travertine systems, are obviously related to the processes responsible for their precipitation and also are extremely important when evaluating analyses of old travertines.

## OVERALL TRENDS

### Water

Changes in the  $\delta^{18}\text{O}$  values of the waters can be due to: (i) degassing of the excess  $\text{CO}_2$  within the waters, (ii) evaporation, (iii) fractionation associated with precipitation of minerals, and (iv) addition of new waters. The sampling program was set-up so that the addition of new waters, *i.e.*, additional springs along the flow path, can be discounted with confidence as a significant factor at most of the systems studied (Durango, Pagosa Springs, Bridgeport, Le Zitelle, and Bagnaccio) and is believed to be responsible for only minor perturbations within the other travertine systems investigated (Narrow Gauge, Honey Creek, and Falls Creek). Degassing of  $\text{CO}_2$  from the waters results in a decrease in  $\delta^{18}\text{O}$  value of the water, as it preferentially removes  $^{18}\text{O}$  from the system. Additionally, almost all of the precipitates that form within the waters within all eight of the systems investigated have higher  $\delta^{18}\text{O}$  values than theoretically expected precipitates at those stations. Thus, due to the effects of degassing as well as precipitation of travertine with higher than equilibrium values, the waters should display a decrease in values downflow. However, all but one of the systems investigated displayed an increase in the  $\delta^{18}\text{O}$  values of the waters downflow. In travertine systems, the lighter isotope is preferentially lost to the waters due to evaporation (Kitano, 1963; Gonfiantini *et al.*, 1968; Friedman, 1970; Usdowski *et al.*, 1979; Michaelis *et al.*, 1985; Turi, 1986; Chafetz *et al.*, 1991a). Hot water travertine systems are especially susceptible to the effects of evaporation due to their elevated temperatures. Therefore, the effects of evaporation on the  $\delta^{18}\text{O}$  values of the waters must be the dominant controlling factor, overshadowing the changes due to degassing and disequilibrium precipitation.

The universally present major increase in  $\delta^{13}\text{C}$  values downflow may be due to: (i) degassing, (ii) fractionation associated with mineral precipitation, (iii) photosynthetic action of green plants, and (iv) addition of new waters. Downflow changes due to disequilibrium fractionation associated with mineral precipitation as well as the addition of new waters may have minor effects on the  $\delta^{13}\text{C}$  values of the waters.

Additionally, studies by Usdowski *et al.* (1979), Dandurand *et al.* (1982), and Lorah and Herman (1988) have concluded that the preferential removal of  $^{12}\text{C}$  by green plants does not affect the overall carbon distribution in a stream. Travertine precipitating springs commonly reach the surface highly charged in dissolved  $\text{CO}_2$  and rapidly degas as a result primarily of the release of hydrostatic pressure (see Chafetz *et al.*, 1991a, fig. 5 (photograph of energetic degassing at a spring orifice) and table 1 (lists of changes in  $P_{\text{CO}_2}$  values downflow)). Chafetz *et al.* (1991a, fig. 7) documented an approximately 5‰ increase in  $\delta^{13}\text{C}$  values through 25 m of flow due to degassing for the springs near Durango, Colorado. Thus, the preferential loss of  $^{12}\text{C}$  due to degassing of  $\text{CO}_2$  (Gonfiantini *et al.* (1968), Hendy (1971), Usdowski *et al.* (1979), Amundson and Kelly (1987), Chafetz *et al.* (1991a)) is believed to be the dominant control on  $\delta^{13}\text{C}$  values of the waters in the systems investigated.

### Precipitates

Downflow within the travertine systems, the stable isotopic composition of the mineral precipitates can differ due to changes in the: (i) water from which they precipitated, (ii) temperature of the water, and (iii) saturation state of the water. As demonstrated and discussed above, the  $\delta^{18}\text{O}$  values of the waters comprising these systems increase downflow, with the exception of Honey Creek (no change) and Falls Creek (small decrease). Thus, if all else were held constant, the precipitates which formed within these waters should display a downflow increase in values. The downflow increase of the  $\delta^{18}\text{O}$  values in the precipitates is well-displayed in the data from Narrow Gauge (Table II), Bridgeport (Table VII), and Le Zitelle (Table VIII, Fig. 9A).

The downflow trend can be complicated because water temperature and level of supersaturation also can significantly affect the  $\delta^{18}\text{O}$  value of the precipitates within travertine systems. The hot water systems tend, though not always, to decrease in temperature as they flow away from their orifice. Thus, the precipitates should increase in  $\delta^{18}\text{O}$  value downflow due solely to temperature changes (Friedman and O'Neil, 1977). However, hot water systems that do not have highly elevated water temperatures at their orifice, as well as many ambient temperature systems, can experience temperature increases downflow due to solar heating, especially during the summertime. For example, the water issues at the springs north of Durango at  $33^\circ$  and can reach at least  $36^\circ$  at the base of flow during the afternoon of the summer months. Thus, the  $\delta^{18}\text{O}$  values of the precipitates can either increase or decrease depending upon the change in temperature of the waters from which they precipitate. In addition to the composition and temperature of the waters, the degree of supersaturation of the waters also can effect the  $\delta^{18}\text{O}$  values of the precipitates. Commonly there is a kinetic inhibition to the precipitation of calcium carbonate within travertine precipitating waters; precipitation generally does not commence until the saturation state of the waters reaches 4 to 10 times saturation (Friedman, 1970; Jacobson and Usdowski, 1975; Dandurand *et al.*, 1982; Usdowski, 1982; Reddy, 1983; Suarez, 1983; Srdoc *et al.*, 1985; Herman and Lorah, 1987, 1988; Utech, 1988; Chafetz *et al.*, 1991a). The waters generally reach the

surface slightly supersaturated with respect to calcite and, due to degassing of  $\text{CO}_2$ , the level of supersaturation increases, sometimes to very high levels, e.g., Tables I, IV and V. With further distance downflow, the rate of precipitation increases, and concomitantly, the level of supersaturation decreases. Consequently, the precipitates form from highly supersaturated waters and as a result are not in stable isotopic equilibrium with the composition of the waters. It has been recognized by Gonfiantini *et al.* (1968), Hendy (1971), Usdowski *et al.* (1979), Dandurand *et al.* (1982), Michaelis *et al.* (1985), Turi (1986), and Chafetz *et al.* (1991a) that as the rate of precipitation increases there is a decrease in the expected equilibrium fractionation between the  $\delta^{18}\text{O}$  values of the water and the precipitate. Thus, the level of supersaturation can affect the stable isotopic composition of the precipitates in a complex manner which will be superimposed upon the general downflow increase in  $\delta^{18}\text{O}$  values due to (i) changes in water composition, and, in hot water systems, (ii) decreases in temperature.

The  $\delta^{13}\text{C}$  values of the waters in all eight systems studied increase downflow and so the values within the mineral precipitates should show a similar overall change. However, the temperature and pH of the waters change downflow within these systems and these variables influence the relative abundance of different ionic species in solution in the water (e.g.,  $\text{CO}_2$ ,  $\text{HCO}_3^-$ , see Friedman, 1970). Changes in the relative abundances of the ionic species could influence the fractionation of  $^{13}\text{C}$  between the water and precipitate (Friedman, 1970). And, as discussed above, the precipitates form from highly supersaturated waters and precipitates from these waters generally do not exhibit the theoretically predicted isotopic equilibrium fractionation (Friedman, 1970; Chafetz *et al.*, 1991a). Thus, whereas the  $\delta^{13}\text{C}$  values of the waters universally display a large increase downflow, the precipitates in essentially all of the systems investigated display a lower per mil increase in  $\delta^{13}\text{C}$  values than the relative increase in the waters. For example, from vent to pool at Narrow Gauge, the  $\delta^{13}\text{C}$  values of the waters exhibit a change of approximately 3.2‰ whereas the precipitates exhibit a change of approximately 2.0‰ through the same interval. This relationship was previously recognized for the Durango deposits (Table III, Chafetz *et al.*, 1991a). Thus, while the  $\delta^{13}\text{C}$  values of the precipitates may get higher downflow (Fig. 9B), they do not necessarily reflect the magnitude of the change displayed by the waters.

#### SMALL SCALE TRENDS

In addition to the overall trends discussed above, consistent differences in composition also occur within travertine systems between constituents which formed in very close proximity to one another. The floating crusts (ice, rafts) form at the air/water interface. Samples which formed within the water column, generally within centimeters of the water surface, were collected from a number of stations immediately subjacent to samples of crusts. The samples consisted of carbonate precipitation on biologic structures, carbonate-encrusted gas bubbles, and precipitates on pieces of copper. The carbonate comprising the crusts essentially always displays higher  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values than the precipitates which

formed within the water column, even though they were only separated by centimeters. This relationship was recognized between pairs of samples from a number of different travertine systems, essentially wherever crusts could be sampled. The  $\delta^{13}\text{C}$  values show a much more pronounced difference between these two suites of samples than do the associated  $\delta^{18}\text{O}$  values. The higher  $\delta^{13}\text{C}$  values for the crusts is probably due to the preferential loss of  $^{12}\text{C}$  due to degassing of the  $\text{CO}_2$  at the air/water interface. The higher  $\delta^{18}\text{O}$  values associated with the crusts may be due to lower water temperatures or selective loss of  $^{16}\text{O}$  due to evaporation at the air/water interface. These crusts sink, commonly due to the effects of rain, and become part of the pool-bottom travertine accumulation along with encrusted biologic structures, carbonate-encrusted gas bubbles, etc. These allochems with distinctly different stable isotopic signatures are deposited together, i.e., crusts sink and accumulate next to encrusted biologic structures and carbonate-encrusted gas bubbles. Thus, analyses of whole-rock samples from the same site will vary depending upon the relative abundance of the different constituents.

Chafetz *et al.* (1991a) have described differences in mineralogy and crystal habit of the precipitates comprising the walls of carbonate-encrusted gas bubbles, another example of differences which can occur through distances on the order of 10's of microns. They interpreted these differences to be the result of changes in the degree of supersaturation of the waters as precipitation occurred. Precipitation of the carbonate-encrusted gas bubbles was observed to occur within a matter of minutes. Their discussion emphasizes the microscopic scale in which significant differences in water chemistry, e.g., level of supersaturation, can occur.

#### Irregular variations

In addition to the "normal" downflow changes described for travertine systems, there are lateral changes which occur because of the vagaries of the flow path of the water. The sampling program was, in general, set-up to evaluate changes in water chemistry with flow. Thus, the main threads of downflow current were sampled at most sites. However, travertine precipitation also actively occurs at sites of slow water flow as well as at stagnant sites. As was obvious at the Narrow Gauge site when sampling, and in the data presented in Tables II and III (e.g., changes in temperature of the water), the water issued from the vent (Fig. 2, station 3) and flowed toward the spillway (station 5) and then down toward the basal pools. Two sites were sampled where the water was either stagnant (station 2) or flowed very slowly (station 4). These stations are situated relatively close to the vent, and yet both stations, and station 2 in particular, display  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values of their precipitates similar to contemporaneous precipitates which formed much further downflow (Table II). The reasons for this are readily apparent at the active site of precipitation. The slowly moving and stagnant waters cooled and degassed prior to the precipitation of the aragonite. However, in the rock record, the increase in  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values relative to distance from the vent would not be apparent. Thus, changes in the stable isotopic composition of the



waters and their precipitates do not necessarily represent the flow distance (as the "crow flies") of the water.

The location of the spring orifice also changes from time to time, especially in a hot water system. And thus, a layer of travertine which was precipitated at some distance downflow from the vent may be covered by a layer which precipitated immediately adjacent to the vent. Succeeding layers can then have significantly different compositions. Additionally, as precipitation occurs and layers build-up, the water path itself migrates even without movement of the vent. All in all, laterally and/or vertically adjacent precipitates may have significantly different compositions because of these types of changes in the flow of the water.

It should be clear from the preceding, that constituents within travertine systems display significant changes in chemical make-up within each system. Thus, it is imperative that one have a good understanding of how a constituent or accumulation of constituents formed before one attributes significance to geochemical analyses of that sample. Composition of constituents vary because of: (i) overall changes with flow (e.g., degassing, temperature, etc.), (ii) microenvironmental controls (e.g., crusts versus precipitates which formed within the water column), and (iii) disequilibrium precipitation. In order to minimize these effects so that the most information can be gleaned concerning conditions at the time of formation, the same type of allochem should be sampled when attempting to evaluate changes in composition either (i) downflow within a travertine system, or (ii) between systems. Additionally, it probably would be best if samples could be taken from immediately adjacent to the orifice as well as at the distal part of the deposit. This would provide the highest chance of obtaining the full range of compositions. It would be best if constituents which precipitated under equilibrium conditions could be sampled; geoscientists studying speothems have long checked their samples for precipitation under equilibrium conditions (Fantidis and Ehhalt, 1970; Hendy, 1971; Thompson *et al.*, 1976). However, a prime criterion used in those studies necessitates isotopic analyses along a single growth layer; whereas this may be feasible for a stalagmite or stalactite, it is very difficult to satisfy this criterion for even a very small travertine accumulation. Thus, interpreting paleoconditions from analyses of ancient travertine deposits will be very risky.

## CONCLUSION

The  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values of the waters from which modern travertines are being deposited vary considerably in both hot water and ambient water travertine systems. Some of the stable isotopic variability within the waters fit trends, e.g.,  $\delta^{13}\text{C}$  values get progressively higher with flow away from the orifice. Even though all of the systems investigated displayed the same downflow trend with respect to  $\delta^{13}\text{C}$  values of the waters, the magnitude of change from orifice to end of travertine precipitation as well as the rate of change varied considerably between systems. In contrast, some large scale variability seems to be the product of the distinctive attributes of individual systems. For example, whereas hot spring deposits all displayed progressively higher  $\delta^{18}\text{O}$  values

downflow, the two ambient systems studied exhibited either no recognizable trend (Honey Creek) or a change to lower  $\delta^{18}\text{O}$  values downflow (Falls Creek).

The stable isotopic composition of the precipitates, similar to the waters from which they precipitated, displayed some overall trends as well as marked variability within very short distances. Some of the variability can be attributed to the processes involved in the precipitation of the particular type of allochem. For example, encrustations on biologic substrates within the water column essentially always displayed lower  $\delta^{13}\text{C}$  values than crusts which formed at the water/air interface immediately superjacent to the biologic structures. Other more randomly appearing differences can be attributed to the vagaries of the flow paths, such as differences observed between laterally adjacent samples collected within the main pool at Narrow Gauge (Fig. 2, stations 2, 3, and 4).

Thus, there are commonly occurring overall changes in the stable isotopic composition of the travertine, some of which display general trends, and there are changes which follow no recognizable trend. Even attributes of the travertine which display general trends, e.g., a progressive increase in the  $\delta^{13}\text{C}$  values of the precipitates downflow, do not display the same magnitude of change as do the waters. The consequence is that the use of compositional data from ancient travertines to interpret the composition of the waters, conditions at the time of deposition, etc., must be used with extreme care.

## ACKNOWLEDGEMENTS

First and foremost, we would like to acknowledge the enthusiastic work of Pat Rush on this project. While as a post-doctoral assistant, he worked with us in the field during 1988 and 1990 at Durango and Pagosa Springs, and during 1990 at Yellowstone National Park. Keith Kilson, as an R.A., assisted with a considerable number of the stable isotopic analyses. We would further like to acknowledge the field assistance of Josh Chafetz at Yellowstone (1991) and at Bridgeport (1992), and Bob Folk and Rachel Eustace, at Viterbo, Italy (1992). Acknowledgment is made to the Donors of The Petroleum Research Fund, administered by the American Chemical Society, for the support of this research to HSC. We are also grateful to reviewers Joyce Lundberg and Andrew S. Goudie for their useful suggestions.

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